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OFFICIAL

METHOD OF MANUFACTURING A TYPE OF OLEFIN OXIDE

Inventors: Yoshisuke Watanabe  
2-29 Chohai-cho, Minami-ku,  
Nagoya-shi  
Kazuhiro Matsuzaki  
4-7 Iwato-cho, Minami-ku,  
Nagoya-shi  
Hiroshi Sugawa  
43-1 Sukuchi, Narumi-cho,  
Midoriku, Nagoya-shi  
Yoshinobu Hirayama  
5 Takiharu-cho, Minami-ku,  
Nagoya-shi  
Applicant: Mitsui Nisso Urethane Co., Ltd.  
4-13-13 Akasaka, Minato-ku, Tokyo

Claim

A method of manufacturing a type of olefin oxide characterized by the fact that, during the manufacture of a type of olefin oxide by the saponification reaction of an olefin chlorohydrin aqueous solution with an alkali while steam is blown, a column type multistage reactor consisting of drip stages is used as the reaction section.

Detailed explanation of the invention

The present invention relates to a method of manufacturing a type of olefin oxide. More specifically, it relates to a method of manufacturing a type of olefin oxide by the saponification reaction of a type of olefin chlorohydrin by using a drip stage column as the saponification reactor.

Conventionally, in the case of the manufacture of ethylene oxide, propylene oxide, epichlorohydrin and other olefin oxides by the chlorohydrin method, first of all, an olefin chlorohydrin aqueous solution is obtained by the reaction of an olefin and chlorine in the presence of water. By adding an alkali such as milk of lime or caustic soda to this aqueous solution and conducting a saponification reaction, an olefin oxide is formed and the olefin oxide is produced by removal and purification from the reaction solution. The olefin chlorohydrin aqueous solution is obtained as a 3% to 6% low-concentration solution mainly to inhibit the formation of dichloro bodies as by-products. Furthermore, the alkali aqueous solution is also used in the reaction as a 10% to 20% aqueous solution. Moreover, if the olefin oxide formed in the reaction is not removed rapidly from the reaction system, the formation of a glycol as a by-product will increase significantly to reduce the olefin oxide yield. Therefore, while a large amount of steam is blown into the reaction solution, the olefin oxide is removed from the reaction system. There is a correlation between the amount of steam and the yield of olefin oxide. If the amount of steam is small, the yield of olefin oxide is decreased. A variety of documents have already clarified this relationship. This is also described in, for example, "Halogenation, dehalogenation and chloromethylation" (by Yoshio Nagai) as Unit Process Series 3 of the Chemical Industry Co. The economical amount of steam to be used is generally 8 tons to 12 tons per ton of olefin oxide. An olefin oxide yield of 93% to 96% is obtained. Furthermore, in a recent report, by using a column type multistage reactor consisting of more than five stages having overflow sections as a saponification vessel, it has been described that a high olefin oxide yield can be obtained in a range of small amounts of steam in British Patent No. 1242041.

As a result of further investigations into the saponification reaction apparatus on the basis of the above fact, the present inventors discovered that, if the main reaction section of the column type stage reactor having overflow sections considered conventionally is made into the drip stage type, the reaction stage is divided, the olefin oxide yield under the same conditions is

increased and operating characteristics are excellent, in comparison to the conventional column type stage apparatus having overflow sections.

As a result of carrying out the saponification reaction according to the present invention by using, for example, a propylene chlorohydrin aqueous solution at a propylene chlorohydrin concentration of 4.50% and 80°C and a milk of lime at a slaked lime concentration of 12.9% and 70°C, although the theoretical amount of steam to be blown as required in the saponification reaction alone was about 2 tons (per ton of propylene oxide), when about 4 tons (per ton of propylene oxide) were used in one stage of the reaction apparatus, the olefin oxide yield was about 93%. If about 6 tons of steam were used, the olefin oxide yield was about 96%. In contrast to this, if an apparatus consisting of more than five stages in the column type stage reaction apparatus having conventional overflow sections was used as a reactor, by using 4 tons (per ton of propylene oxide) of steam, propylene oxide yield was about 98%. It was confirmed that the column type reaction apparatus is more advantageous. However, in the case of carrying out the reaction in the column type multistage reactor consisting of stages having overflow sections, because of plugging inside the column due to the use of milk of lime, flooding, foaming due to alkali and so on, the operating characteristics of the column are poor. Therefore, the interstage distance has to be increased. In actual practice, having a column type reactor of more than four stages leads to an escalation of the construction cost and is not common. Furthermore, with column type reactors of more than five stages, in the case of using milk of lime, in particular, plugging inside the column is frequent. There are many cases in which plants are frequently shut down. The present inventors provide a new method for the manufacture of a type of olefin oxide by using drip stages in reaction stages as a column type multistage reactor without these disadvantages.

The first effect of the present invention is the fact that the reaction is divided into multiple stages. In other words, in the case of a column type multistage reactor consisting of stages having overflow sections, the reaction solution flows from the feed inlet or spout toward the overflow section and falls to the next stage. The residence time of the solution is long. On the other hand, since the saponification proceeds at a high rate, most of the reaction occurs between the feeding stage and the next stage. In particular, in the feeding stage, foaming is vigorous due to excess alkali and it is necessary to adopt a large interstage distance. However, in the case of using the drip stages of the present invention, since the reaction solution moves little on the stage, the residence time of the solution in each stage is short. Therefore, the reaction can be conducted by division into multiple stages instead of the feeding stage alone. Thus, the interstage distance of reaction stages can be decreased. Furthermore, in the case of a column type multistage reactor consisting of stages having overflow sections, with the consideration of the foaming due to alkali in the feeding stage mentioned previously, the supplying of the feed

solution by dividing into several stages is conducted. Comparing the case of supplying the feed solution in five stages and the case of supplying the feed solution to the uppermost stage using five drip stages in the present invention, as a result of conducting the saponification reaction with the same amount of steam blown, the olefin oxide yield is increased by about 0.5% for the latter case. The reason is believed to be due to the fact that the reaction in the latter case is spread across multiple stages but the absorption of the feed solution sensible heat occurs only in the feeding stage. Therefore, in the stages other than the feeding stage, the blown steam is used as stripping steam to the maximum effectiveness.

The second effect of the present invention is to make the column compact. In the stage column having overflow sections, since the solution falls to the lower stage through the overflow section, it is necessary to increase the overflow section area ratio in order to improve falling with respect to the foaming solution. In contrast to a decrease in the effective area of the stage and an increase in the column diameter, in the case of the drip stage column, the effective area of the stage is increased since there is no overflow section. Furthermore, for saponification, since the reaction occurs in the overflow section, it is accompanied by foaming in the case of a vigorous reaction. Thus the solution flow is hindered and this becomes a cause of flooding. With the drip stage column, there is no such a problem. Furthermore, in the case of using a slurry solution such as milk of lime as an alkali solution, there is no dead space in the stage when there is no overflow section. Finally, there is an advantage of having no residence of the slurry. Moreover, as an advantage in the apparatus efficiency, in the case of the drip stage, the superficial column velocity can reach 5 m/sec. This means that the superficial column velocity is more than four times that of the stage type having the conventional overflow section. In addition, the especially advantageous point of the present saponification reaction is that, in the case of using a drip stage with an aperture area ratio greater than 30%, in contrast to the minimum superficial column velocity of 1 m/sec or so in the case of the stage column having the overflow section, the stage constitution is possible during the reaction even if it is 0.2 m/sec due to a reduction in the apparent specific gravity in the stage because of foaming and the surface tension due to the alkali. In other words, this column is stable over a wide operating range. The saponification reactor can be made very compact. Furthermore, in the case of carrying out the saponification reaction with a column, in regard to the usage of the drip stage in the upper stage because of an increase in the superficial column velocity in the upper stage due to the olefin oxide generated, the operability is conventionally improved in comparison to the stage having the overflow section.

As the trays of the drip stages of the drip stage type multistage saponification reactor of the present invention, sieve trays can be used preferably. In this case, the aperture diameter is preferably 3 mm to 20 mm and the aperture area ratio is preferably 20% to 60%. In regard to the

aperture diameter in the case of the sieve tray, it is necessary to select the optimum diameter according to the alkali solution used and the column diameter. Especially in the case of using milk of lime or other slurry solutions as the alkali solution, a higher value in this range is preferred. Furthermore, the aperture area ratio varies with the vapor superficial column velocity, the number of stages, and the position of the stage. In the case of a high vapor superficial column velocity, a higher value in this range is also preferred. Furthermore, in the case of a large number of stages, it is also preferable that the aperture area ratio is a lower value in this range. Moreover, in regard to the relationship between the position of the stage and the aperture area ratio, it is desirable that the aperture area ratio is a higher value in this range than that in the stage with a higher reaction ratio. In other words, in the design of the drip stage in the present invention, the optimum design value can be determined by setting the solution-loading amount and the feed solution temperature and setting the olefin oxide yield. In general, in the case of a vapor superficial column velocity of 1.5 m/sec to 2.5 m/sec, there are 3 to 5 drip stages. As the drip stage, a sieve tray is used. It is desirable that the aperture area ratio is set at 30% to 50% with an aperture diameter of 7 mm to 15 mm. It goes without saying that, for the recovery stage other than the main reaction stage, the column diameter has to be increased so that the superficial column velocity is less than 1.5 m/sec in this case. Furthermore, in the case of using a sieve tray as the drip stage with a superficial column velocity of 0.5 m/sec to 1.5 m/sec, it is desirable to set the aperture diameter of the sieve tray at 5 mm to 12 mm and the aperture area ratio at 20% to 40%.

Next, an example of the method of the present invention will be explained on the basis of a diagram.

The olefin chlorohydrin aqueous solution (1) and the alkali aqueous solution (2) are mixed and introduced to the top stage of a drip stage type multistage saponification apparatus (6). In this diagram, the stage constitution of (6) consists of four stages of the drip stage section (7), two stages of the recovery section (8), and a pot section (9). Steam (3) for use in stripping the olefin oxide is blown into the pot section solution. The saponification waste solution (4) is discharged out of the system while adjustment is made so that the pot section solution plane remains constant. Furthermore, the reaction olefin oxide gas rises inside the column together with the unreacted olefin chlorohydrin and steam and enters the partial condenser (10) on the top. Here, most of the unreacted olefin chlorohydrin and a portion of the steam are condensed and are recycled into the reaction system. The raw olefin oxide gas (5) containing most of the olefin oxide gas formed is withdrawn from the system. As shown by (7) of this diagram, the feeding stage and several of its lower stages with vigorous reaction are drip stages. With these stages, the effectiveness described previously is obtained. Of course, this diagram is an example. It is also possible to change the column diameter and height of each stage according to the superficial

column velocity in each section, the foaming extent, etc. There are many cases in which they are effective with these changes. In addition, it is also acceptable to install enriching stages above the feeding stage to carry out enriching of the olefin oxide in the same manner.

Next, an explanation will be given in regard to application examples for the case of the manufacture of a type of olefin oxide using the present apparatus.

#### Application Example 1

Sieve plates with an aperture diameter of 10 mm and an aperture area ratio of 30% were used in the drip stage section of a drip stage type multistage saponification reaction apparatus that had an interstage distance of 600 mm and four stages. In the recovery section, sieve plates with an aperture diameter of 10 mm and an aperture area ratio of 12% were used, and there were two stages with an interstage distance of 400 mm. Overflow sections with an area ratio of 15% were provided. The column diameter was 300 mm in all cases. In the present apparatus, a 4.50% propylene chlorohydrin aqueous solution at 80°C and a flow rate of 1457 kg/h and a 12.9% slaked lime aqueous solution at 70°C and a flow rate of 451 kg/h were charged. From the pot section of the saponification apparatus, steam at 3 kg/cm<sup>2</sup> and 118 kg/h was blown and the saponification reaction was conducted. At this time, operating conditions were adjusted so that the pot section temperature was 102°C and the temperature of the distilled raw propylene oxide gas was 70°C. As a result, the propylene glycol content in the saponification waste solution was 408 ppm and 39.6 kg/h were obtained as pure propylene oxide. The yield of the propylene oxide was 98.3%.

#### Application Example 2

With the same apparatus and the same raw materials as in Application Example 1, the propylene chlorohydrin aqueous solution at 5088 kg/h, the slaked lime aqueous solution at 1576 kg/h and steam at 412 kg/h were charged, and the same reaction was conducted. As a result, the propylene glycol content in the saponification waste solution was 275 ppm and 139.0 kg/h were obtained as pure propylene oxide. The yield of the propylene oxide was 98.9%.

#### Application Example 3

With the same apparatus and the same raw materials as in Application Example 1, the propylene chlorohydrin aqueous solution at 10918 kg/h, the slaked lime aqueous solution at 3381 kg/h and steam at 884 kg/h were charged, and the same reaction was conducted. As a result, the propylene glycol content in the saponification waste solution was 390 ppm and 297.0 kg/h were obtained as pure propylene oxide. The yield of the propylene oxide was 98.5%.

#### Application Example 4

Sieve plates with an aperture diameter of 15 mm and an aperture area ratio of 40% were used in the drip stage section of a drip stage type multistage saponification reaction apparatus that had an interstage distance of 500 mm and four stages. In the recovery section, sieve plates with an aperture diameter of 10 mm and an aperture area ratio of 12% were used, and there were two stages with an interstage distance of 400 mm. Spouts with an area ratio of 15% were provided. The column diameter was 300 mm for the drip stage section and 400 mm under the recovery section. With the same raw materials as in Application Example 1, the propylene chlorohydrin aqueous solution at 21827 kg/h, the slaked lime aqueous solution at 6758 kg/h and steam at 1767 kg/h were charged, and the saponification reaction was conducted. As a result, the yield of propylene oxide was 98.4%. The propylene glycol content in the saponification waste solution was 400 ppm and about 593 kg/h of pure propylene oxide were obtained.

#### Application Example 5

As a result of increasing the amount of steam blown to 549 kg/h in the experiment in Application Example 2, the yield of propylene oxide was 99.1%. The propylene glycol content in the saponification waste solution was 220 ppm.

#### Application Example 6

Sieve plates with an aperture diameter of 10 mm and an aperture area ratio of 30% were used in the drip stage section of a drip stage type multistage saponification reaction apparatus that had an interstage distance of 500 mm and five stages. In the recovery section, sieve plates with an aperture diameter of 10 mm and an aperture area ratio of 12% were used, and there were three stages with an interstage distance of 400 mm. Overflow sections with an area ratio of 15% were provided. The column diameter was 300 mm. With this apparatus, as a result of blowing of the same feed materials and steam under the same conditions as in Application Example 5, the yield of propylene oxide was 99.5%. The propylene glycol content in the saponification waste solution was 160 ppm.

#### Application Example 7

Using the apparatus of Application Example 1, a 6% dichlorohydrin aqueous solution at 80°C and 6100 kg/h and a 12.9% slaked lime aqueous solution at 70°C and 1874 kg/h were charged into the saponification reactor. As a result of blowing steam at 835 kg/h, the glycol content in the saponification waste solution was 450 ppm. Pure epichlorohydrin was obtained at 258 kg/h. The saponification reaction yield was 98.5%.



### Application Example 8

Using the apparatus of Application Example 6, charging the raw materials under the same conditions as in Application Example 7 and as a result of blowing steam at 1112 kg/h, the glycol content in the saponification waste solution was 210 ppm. Pure epichlorohydrin was obtained at 261 kg/h. The saponification reaction yield was 99.3%.

### Comparative Example 1

In a stage column with a column diameter of 300 mm, an overflow section area ratio of 15% in each stage, consisting of five stages of sieve plates with an aperture area ratio of 12% and an aperture diameter of 10 mm from the top with an interstage distance of 500 mm and three stages with an interstage distance of 400 mm underneath, the propylene chlorohydrin aqueous solution at 5088 kg/h, the slaked lime aqueous solution at 1576 kg/h and steam at a blow-in amount of 549 kg/h were charged under the conditions of Application Example 5. The foaming of the feeding stage reached more than 500 mm immediately after feeding and flooding occurred. Steam gushed out from the bottom.

### Comparative Example 2

The same test as in Comparative Example 1 was conducted except that the stage height of the feeding stage of the column in Comparative Example 1 was 2000 mm. As a result, the foam height was between 1000 and 1500 mm, and operation was impossible for about 30 min. Foaming occurred inside the overflow sections in three stages under the feeding stage. A gradual flooding trend was observed. After 40 min, flooding did occur.

### Comparative Example 3

Using the column in Comparative Example 2, the propylene chlorohydrin aqueous solution at 2544 kg/h, the slaked lime aqueous solution at 788 kg/h and steam at a blow-in amount of 274 kg/h were charged. As a result, foaming of the feeding stage was 850 mm and a generally stable operation could not be conducted. The propylene glycol content in the saponification waste solution at this time was 270 ppm.

### Comparative Example 4

Among the conditions of Comparative Example 2, the propylene chlorohydrin aqueous solution was dispersed at 1018 kg/h x 5 stages each and the slaked lime aqueous solution at 312 kg/h x 5 stages each and charged into the column of Comparative Example 2. Although a stable operation was conducted, the propylene glycol content in the saponification waste solution

was 420 ppm and the propylene oxide yield was 98.3%. Compared with Application Example 5, the propylene oxide yield is 1% lower.

Brief description of the figures

Figure 1 shows an example of a column type multistage reactor with the reaction section consisting of drip stages.

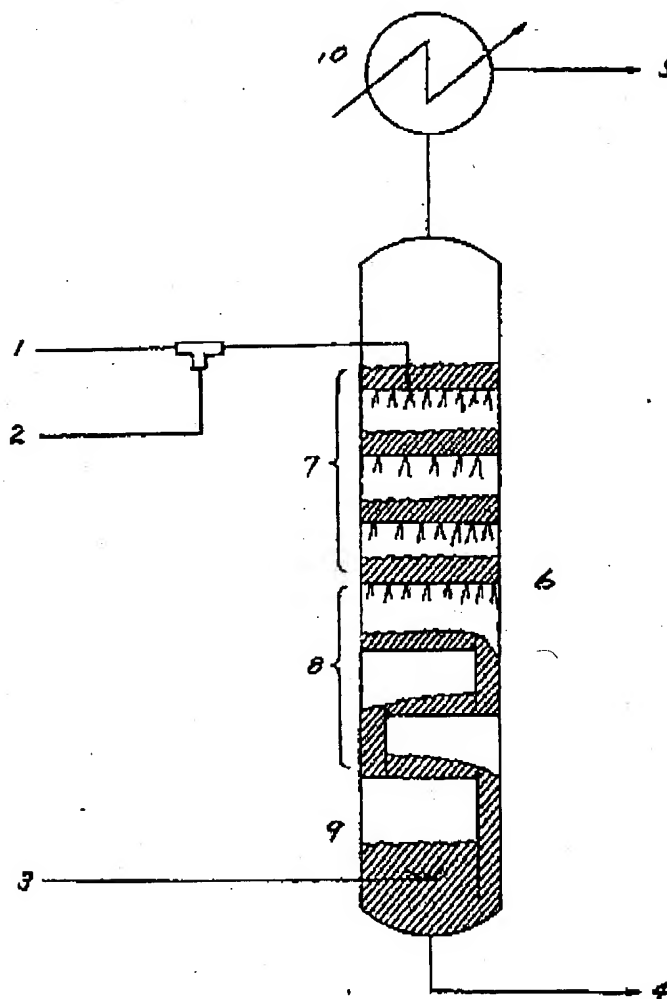


Figure 1